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(54) Title: HIGH PERMEABILITY, LOW ABSORPTION CAPACITY POLYMERS

(57) Abstract: An improved process for the preparation of superabsorbent polymers having high gel bed permeability and low absorption capacity, and the polymers prepared by the process. More specifically, the process is a process for the preparation of water-swallowable, water-insoluble polymer particles having high gel bed permeability and low absorption capacity, the process comprising crosslinking the polymer using at least two covalent crosslinking agents under conditions such that there is formed a polymer which is substantially uniformly crosslinked and which has a gel bed permeability of at least $5 \times 10^{-9} \text{ cm}^2$ and an absorption capacity of less than 26 g/g. The present invention includes articles containing the high permeability and low absorption capacity polymer.

HIGH PERMEABILITY, LOW ABSORPTION CAPACITY POLYMERS

This invention relates to superabsorbent polymer (SAP) compositions and a process for preparing said compositions.

5 Superabsorbent polymers are well-known materials that commonly are used in personal care articles such as diapers. These polymers are known to absorb several times their weight of, for example, water, saline solution, urine, blood, and serous bodily fluids.

Gel blocking is a well-known problem associated with the use of superabsorbent polymers in absorbent articles, such as diapers. Gel blocking occurs when
10 rapid expansion of superabsorbent polymer particles around the point of entry of body fluid into an absorbent article causes a closing of the interstitial spaces and pores in the SAP-fluff matrix. Since the transport of liquid by diffusion through a swollen hydrogel is much slower than transport through the interstitial spaces, a sealing effect occurs in the area of fluid entry. This effect is referred to as "gel blocking." Subsequent amounts of fluid can no
15 longer penetrate into the absorbent core and tend to flow in an uncontrolled manner across the surface of the already superficially saturated area to its edge, resulting in undesirable leakage from the absorbent article.

One way of combating gel blocking is to increase the permeability of the superabsorbent polymer gel bed. Since superabsorbent polymers with lower absorption
20 capacities tend to have higher permeability, another way of combating gel blocking is to decrease the absorption capacity of the superabsorbent polymer.

It is well known in the art that the absorption capacity of the superabsorbent polymer is a function of the amount of polyvinyl crosslinking agent added during the polymerization (see Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer
25 Technology," John Wiley & Sons, 1998), with greater amounts of polyvinyl crosslinker giving lower levels of absorption capacity. Unfortunately, it is difficult to achieve levels of absorption capacity sufficiently low to reduce gel blocking, without the use of a large excess of polyvinyl crosslinking agent or additional process steps such as particle surface crosslinking. Unfortunately, polyvinyl crosslinking agents are too expensive to use in large
30 amounts. Additional process steps, such as particle surface crosslinking steps, have associated disadvantages such as extra capital and operating costs.

It is also known in the art that water-soluble carboxylic acid-containing polymers can be crosslinked by means of esterification with, for example, relatively inexpensive polyhydroxy substances. Sometimes this is referred to as curing. Other
35 reactions are also known for this purpose, such as amidation of the carboxylic acid-

containing polymer with a polyamine substance. Typically, these esterification type reactions require dehydrating conditions, and do not readily occur during the polymerization step of the process due to the high water content of the reaction solution. Rather these dehydrating reactions occur mostly during the drying step of the process.

5 WO 95/26209 discloses that the gel bed permeability can be increased by using a larger particle size distribution and by using surface crosslinked superabsorbent polymers. Unfortunately, preparing surface crosslinked superabsorbent polymer entails additional process steps, thereby adding to the manufacturing costs of the superabsorbent polymer.

10 It would be desirable to have an improved, simpler process for preparing a superabsorbent polymer having high gel bed permeability and low absorption capacity that would not require a surface crosslinking step or large amounts of costly polyvinyl crosslinker. One clear advantage of such a process would be the cost savings associated with eliminating processing steps.

15 The present invention includes an improved process for the preparation of superabsorbent polymers having high gel bed permeability and low absorption capacity, and the polymers prepared by the process. More specifically, the process is a process for the preparation of water-swellaable, water-insoluble polymer particles having high gel bed permeability and low absorption capacity, the process comprising crosslinking the polymer
20 using at least two covalent crosslinking agents under conditions such that there is formed a polymer that is substantially uniformly crosslinked and that has a gel bed permeability of at least $5 \times 10^{-9} \text{ cm}^2$ and an absorption capacity of less than 26 g/g. The polymer of the invention is the polymer prepared by the process of the invention. The present invention includes articles containing the high permeability, low absorption capacity polymer.

25 We have found that in a bulk, or solution, polymerization process for a superabsorbent polymer it is undesirable to provide substantially all of the crosslinks by a curing-like process (as described above) because the crosslinks are generally not incorporated during the polymerization stage, but rather are incorporated only after the removal of a substantial amount of the water from the polymerized gel. The handling of the
30 essentially uncrosslinked polymer gel is much more difficult, and less economical as a result of the high viscosity, but low elasticity, of the gel prior to the esterification reaction (or other curing-like reaction). In contrast, the handling of a crosslinked gel in a bulk, or solution polymerization process is easier by virtue of the mostly elastic, less viscous behavior of the polymer gel. For example, the breaking of the water-containing polymer gel

into smaller, distinct pieces that dry more efficiently is much improved in the mostly elastic state, compared to the mostly viscous state.

The two covalent crosslinking agents include a first crosslinking agent, which is a polyvinyl compound, and a second crosslinking agent, which is a hydroxyl-containing crosslinking compound. The two covalent crosslinking agents crosslink the carboxylic acid-containing polymer in essentially separate stages of the polymer preparation process, namely, the polymerization stage for the first crosslinking agent and the heated drying stage for the second crosslinking agent.

Examples of compounds suitable for use as the first crosslinking agent include compounds having in one molecule 2 to 4 groups selected from the group consisting of $\text{CH}_2=\text{CHCO}-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-$ and $\text{CH}_2=\text{CH}-\text{CH}_2-$. Exemplary first crosslinking agents include: diacrylates and dimethacrylates of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane and pentaerythritol; triacrylates and trimethacrylates of trimethylolpropane and pentaerythritol; highly ethoxylated trimethylol propane triacrylate; tetracrylate and tetramethacrylate of pentaerythritol; allyl methacrylate; and tetraallyloxyethane.

The second covalent crosslinking agent suitably is a hydroxyl-containing crosslinking agent containing at least one hydroxyl functionality suitable to react with a carboxyl moiety on the backbone of the water-swellaable, water-insoluble polymer; provided, however, that the second covalent crosslinking agent has at least two functional groups capable of forming covalent bonds with the superabsorbent polymer. The hydroxyl functionality of the second crosslinking agent is activated by heating the polymer to make an ester with the hydroxyl functionality, for example, during the drying process. This second crosslinker may be a polyol and contain more than one hydroxyl functionality to achieve crosslinking. Optionally the second crosslinker may be a so-called dimodal crosslinker, and employ one or more hydroxyl groups with one or more ethylenically unsaturated groups in the same agent. Mixtures of second crosslinking agents can be employed. For example, it is possible to employ one or more polyhydroxy crosslinkers with one or more dimodal crosslinkers as the second crosslinking agent of the invention.

Examples of polyhydroxy compounds suitable for use as the second crosslinking agent include, but are not limited to, glycerin, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, polyglycerin, trimethylolpropane, polyethylene glycol, and polypropylene glycol-polyethylene glycol copolymers. Examples of dimodal agents suitable for use as the

second crosslinker include, but are not limited to, 2-hydroxyethyl (meth)acrylate, polyethylene glycol monomethacrylate, glycidyl methacrylate, and allyl glycidyl ether. Many examples of this type of dimodal monomer are given in U.S. Patents 4,962,172 and 5,147,956, the teachings of which are incorporated herein by reference. The second
5 covalent crosslinking agent can be employed either neat or as an aqueous solution.

The second crosslinker may be added during the makeup of the monomer mix or at any subsequent stage of the process prior to the drying step of the polymer gel, and serves to crosslink the polymer during or after the drying step. Both the first and second crosslinking agents are employed as bulk, as opposed to surface, crosslinking agents.
10 Accordingly, the polymers of the invention are substantially homogeneously crosslinked, or bulk crosslinked, as opposed to being surface crosslinked. As a result of employing the process of the invention, a relatively low absorption capacity superabsorbent polymer may be prepared without the excessive expense of using large amounts of a more costly polyvinyl crosslinking agent, without the use of expensive surface crosslinking processes
15 and capital outlays, and while avoiding the process handling difficulties of crosslinking an essentially soluble polymer with a curing-like reaction. It is noted that a further surface crosslinking step can optionally be employed in the process of the invention, if further modification of polymer properties is desired.

In one embodiment of the invention both the first covalent crosslinking agent
20 and the second covalent crosslinking agent are present in the polymerization mixture to prepare the polymer of the invention. In another embodiment of the invention, the polyol crosslinking agent can be added to the polymer hydrogel after polymerization is complete or substantially complete but prior to drying of the hydrogel.

The total amount of crosslinking agents to employ generally is determined by
25 the desired degree of gel bed permeability. The crosslinking agents preferably are present in an amount effective to produce a polymer having a gel bed permeability of at least 5×10^{-9} cm² and a absorption capacity of less than 26 g/g. If the total amount of crosslinking agents employed is an amount less than 0.0005 part by weight per 100 parts monomer, the gel bed permeability of the polymer usually is too low and the absorption capacity of the polymer
30 too high. The first crosslinking agent suitably is employed in amounts ranging from 0.0005 to 5 parts by weight per 100 parts by weight of α,β -ethylenically unsaturated monomer used. More preferably, the amount of the first crosslinking agent ranges from 0.1 to 1 part by weight per 100 parts by weight of the α,β -ethylenically unsaturated monomer. The second crosslinking agent suitably is employed in amounts ranging from 0.0005 to 5 parts by
35 weight per 100 parts by weight of α,β -ethylenically unsaturated monomer used. More

preferably, the amount of the second crosslinking agent ranges from 0.1 to 2 parts by weight per 100 parts by weight of the α,β -ethylenically unsaturated monomer.

The hydrophilic polymers of the invention can be prepared from water-soluble α,β -ethylenically unsaturated monomers such as monocarboxylic acids, polycarboxylic acids, acrylamide and their derivatives. Examples of suitable monomers for the preparation of the polymer of the invention include α,β -ethylenically unsaturated monomers such as, for example, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid and alkali metal salts and ammonium salts thereof; itaconic acid, acrylamide, methacrylamide and 2-acrylamido-2-methyl-1-propane sulfonic acid and its salts. Preferred monomers include acrylic acid and methacrylic acid and their respective salt forms, such as alkali metal or ammonium salts. The water-soluble monomers useful in the present invention may be used in amounts ranging from 10 percent to 80 percent by weight based on the total weight of the aqueous monomer solution. Preferably, the amount ranges from 15 percent to 60 percent based on the total weight of the aqueous monomer solution.

Optionally, minor amounts of other water-soluble, unsaturated monomers, such as alkyl esters of the acid monomers, for example, methyl acrylate or methyl methacrylate may be present in the water absorbent polymer. In addition, certain grafting polymers, such as, for example, polyvinyl alcohol, starch and water soluble or swellable cellulose ethers may be employed to prepare products having superior properties. Such grafting polymers, when employed, are used in amounts up to 10 weight percent based on the α,β -ethylenically unsaturated monomer.

The polymerization may be carried out using acid monomers that are not neutralized or that have been neutralized or partially neutralized prior to the polymerization. Neutralization is conveniently achieved by contacting the aqueous monomer with an amount of basic material sufficient to neutralize between 20 and 95 percent of the acid groups present in the acid monomers. Preferably, the amount of basic material will be sufficient to neutralize between 40 percent and 85 percent, and most preferably between 55 percent and 75 percent of the acid groups present in the acid monomers.

Compounds which are useful to neutralize the acid groups of the monomer are typically those which will sufficiently neutralize the acid groups without having a detrimental effect on the polymerization process. Examples of such compounds include alkali metal hydroxides, and alkali metal carbonates and bicarbonates. Preferably, sodium or potassium hydroxides or carbonates are employed to neutralize the monomer. In determining the desired degree of neutralization, care must be taken to ensure that the pH of the resulting crosslinked absorbent polymer, which will be contacted with or dispersed in an

aqueous fluid to be absorbed, is maintained in a range appropriate for the applications for which the polymer is intended. Alternatively, the polymerization may be carried out employing unneutralized monomers and thereafter neutralizing, as is known in the art.

5 If desired, hydrogen peroxide, (0-500 ppm based on acrylic acid) can be added as a bleaching agent either before or after the addition of the neutralizing agent.

Conveniently, a free radical polymerization initiator is used in the polymerization of the water-soluble monomers and the crosslinking agent. A free radical polymerization initiator which is sufficiently soluble in the monomer solution to initiate polymerization is preferred. For example, water soluble persulfates such as potassium persulfate, ammonium persulfate, sodium persulfate, and other alkali-metal persulfates, 10 hydrogen peroxide and water soluble azo-compounds such as 2,2'-azobis-(2-amidinopropane) hydrochloride may be used. Some of these initiators, such as hydrogen peroxide, can be combined with reducing substances such as sulfites or amines to form known redox type initiators. The total amount of initiators used may range from 0.01 to 1.0 weight percent, preferably 0.01 to 0.5 weight percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants. 15

The water-absorbent resin will preferably be lightly covalently crosslinked to render it water-insoluble and water-swelling. The desired crosslinked structure may be obtained by crosslinking the polymer using at least two covalent crosslinking agents that 20 operate by different mechanisms. The first crosslinking agent suitably is a polyethylenically unsaturated crosslinking agent, which is also referred to herein as a polyvinyl crosslinking agent. It is possible to employ two or more different polyvinyl crosslinking agents as the first crosslinking agent of the invention.

While the crosslinking agents will typically be soluble in the aqueous 25 solution of the α,β -ethylenically unsaturated monomer, the crosslinking agents may be merely dispersible in such a solution without negative implications. The use of such dispersing agents is disclosed in U.S. Patent 4,833,222, the teachings of which are incorporated herein by reference. Suitable dispersing agents include carboxymethyl cellulose suspending aids, methyl cellulose, hydroxypropyl cellulose, and polyvinyl alcohol. 30 Such dispersing agents are typically provided at a concentration between 0.005 and 0.1 weight percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

In a preferred embodiment for making polymers useful in the practice of this invention, an aqueous solution of the α,β -ethylenically unsaturated monomer in the partially 35 neutralized form, the covalent crosslinking agents, the initiator and a grafting polymer

substrate, if desired, is prepared. The polymerization of the mixture may be initiated by elevating the temperature of the mixture containing the initiator or by using a redox-type initiator as described above. Generally, the temperature at which polymerization will begin ranges from 5°C to 45°C. The temperature at which the polymerization is carried out is
5 highly dependent on the type of monomers used and the specific initiator system employed. Preferably, the maximum temperature of polymerization ranges from 50°C to 100°C, most preferably from 60°C to 100°C.

Continuous and batch processes for preparing water-swellable, water-insoluble polymers, including gel and suspension polymerization processes, are well known.
10 See, for example, U.S. Patents 4,286,082; and 5,145,906, the teachings of which are incorporated herein by reference. In addition, see Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998). Preferably, the polymer of the invention is prepared in the substantial absence of high temperature oxidizing agents, such as bromine and chlorine oxidizing agents including, for example,
15 sodium chlorate. The process of the invention preferably is a bulk, gel, or solution, polymerization process.

The resultant polymer is typically pre-sized and dried using means well-known in the art. Examples of suitable drying means include fluidized bed driers, rotary driers, heated screw conveyors, forced air ovens and through-circulation belt dryers. Multi-
20 stage drying, in which drying occurs in two or more stages, optionally can be employed.

The composition of the invention exhibits a high gel bed permeability and low absorption capacity. Suitably, the composition has a gel bed permeability, as measured according to the method described below and expressed in square centimeters, of at least 5×10^{-9} , preferably 20×10^{-9} , more preferably at least 30×10^{-9} , even more preferably at least 50×10^{-9} and most preferably at least 65×10^{-9} . In addition, the composition has an absorption
25 capacity, as measured according to the method described below and expressed in g/g, of less than 26, more preferably less than 24, and most preferably less than 22. Compositions having an absorption capacity of less than 20 g/g, and compositions having an absorption capacity of less than 18 g/g can also be prepared. The polymer of the invention may be
30 porous or nonporous.

Preferably, at least 0.01 equivalent of carboxyl groups are present per 100 grams of the water-absorbent resin. Among preferred carboxyl-containing water absorbent polymers are hydrolyzates of starch-acrylonitrile graft copolymers, partially neutralized products of starch-acrylic acid or polyvinyl alcohol graft copolymers, saponification
35 products of vinyl acetate acrylic ester copolymers, derivatives of copolymers of isobutylene

and maleic anhydride, hydrolyzates of acrylonitrile copolymers, crosslinked products of hydrolyzates of acrylonitrile copolymers, crosslinked carboxymethyl cellulose, polyaspartate hydrolyzates of acrylamide copolymers, crosslinked products of hydrolyzates of acrylamide copolymers, partially neutralized products of polyacrylic acids and crosslinked products of partially neutralized polyacrylic acids.

The composition of the invention can optionally include other additives such as, for example, dedusting agents and anticaking agents, perfumes, and various salts. Anticaking agents and dedusting agents are well-known. For example, the cationic surfactant anticaking agents of U.S. Patent 5,728,742 can also be employed. Silica is an example of a preferred anticaking agent. Hydrophilic or hydrophobic dedusting agents, such as those described in U.S. Patents 6,090,875 and 5,994,440, may be added to control the level of dust. Water soluble salts of aluminum, such as aluminum sulfate, may also be employed in the process of the invention. If employed, from 0.25 to 4 weight parts of the aluminum salt preferably are employed per hundred weight parts of dried polymer.

Drying is preferably carried out at a temperature of at least 170°C, more preferably of at least 180°C. Drying is preferably carried out at a temperature of less than 250°C, more preferably less than 200°C. The method of drying is not critical. If desired, the dried polymer may be remoisturized for ease in handling.

Following the completion of drying, the polymer is further sized to form particles preferably having an average diameter less than 2 mm and more preferably less than 1 mm. Preferably, the final polymer product has an average particle size of at least 160 microns.

The superabsorbent polymers of this invention are useful in the manufacture of moisture absorbent articles, such as disposable diapers, sanitary napkins, incontinence garments and bandages. The superabsorbent compositions of this invention are particularly useful in the manufacture of thin and ultra thin disposable diapers which have excellent moisture absorbence capacity, fluid distribution properties and reduced leakage. Construction of diapers and other absorbent articles is well known, and materials useful as fluff in absorbent articles are also well known. For the purposes of the present invention, the term "fluff" is given its meaning as understood by those of ordinary skill in the art. Examples of fluff include cotton fibers, curly fibers, wood pulp fibers, synthetic fibers, or a combination thereof, which are formed into a pad and absorb primarily by capillary attraction mechanism. See, for example, WO 95/26209.

In making absorbent articles with the compositions of this invention, the superabsorbent composition may be mixed with, attached to, layered in, or dispersed in a

porous matrix of fibers. Such matrices are made with hydrophilic fibers such as wood pulp or fluff, cotton linters, and synthetic fibers or a mixture of the fibers and the wood fluff. The fibers can be loose or joined as in nonwovens. Examples of synthetic fibers include those made using polyethylene, polypropylene, polyesters, and copolymers of polyesters and polyamides. The synthetic fibers may be meltblown fibers or fibers which have been treated to render them hydrophilic.

Absorbent articles, such as disposable diapers, typically are made with a liquid-impermeable backing material, a liquid-permeable bodyside facing material and the liquid-absorbing composite sandwiched between the backing material and the facing material. The liquid-impermeable backing material can be made from commercially available polyolefin film and the liquid-permeable facing material can be made from a commercially available nonwoven material, such as spunbonded or corded fibrous web which is wettable and capable of passing urine.

The superabsorbent polymers of the invention can constitute from 5 percent to 95 percent by weight of the absorbent articles of the invention. In a typical absorbent article, the superabsorbent polymer of the invention is dispersed in a fiber matrix: in such an article the superabsorbent advantageously is present in an amount from 30 to 70 weight percent based on the weight of the article and the fiber matrix is present in an amount of from 70 to 30 weight percent based on the weight of the article. In another form of absorbent article, the superabsorbent may be present in a containment structure in which the superabsorbent polymer is present in an amount of 30 to 95 percent by weight. Combinations of dispersed superabsorbent polymer and contained superabsorbent polymer are also known.

The following examples and comparative experiments are given to illustrate the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated.

Absorption capacity (AC) is measured according to the method stated in Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998), page 153.

Substantially homogeneous or uniform crosslinking of the polymer of the invention is determined by analysis of the dependence of the absorption capacity on particle size as described by Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998), pages 192 to 193. Homogeneously crosslinked polymers show essentially no, or only slight, dependence of the absorption capacity on particle size while structured polymer particles, such as surface crosslinked polymers, show

a decrease in absorption capacity with decreasing particle size for at least a part of the particle size range.

Gel bed permeability is measured under a 0.3 psi load using 0.9 percent saline solution on a 40-50 mesh particle size cut by the method described in Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998), page 161.

Procedure A - Polymer Preparation Process

Into an appropriate vessel were added 347 parts of glacial acrylic acid, 331 parts of water, 0.43 parts of VERSENEX 80 (The Dow Chemical Company), and 0.25 - 5 parts of highly ethoxylated trimethylolpropane triacrylate (SARTOMER #9035, Sartomer). The mixture was agitated until homogeneous, and then 580.4 parts of a 28.5 percent aqueous solution of sodium carbonate was added. The carbon dioxide generated by the neutralization of the acrylic acid was allowed to vent from the vessel.

Hydrogen peroxide, (200 ppm based on acrylic acid) was added before the addition of the carbonate solution.

The solution was transferred to an appropriate vessel equipped with an agitator capable of tearing the polymerization gel mass. The agitator was started and 5.5 parts of a 10 percent aqueous solution of sodium persulfate was then added. The mixture was sparged with nitrogen for 10-60 minutes at a rate sufficient to remove dissolved oxygen from the solution. The mixture was warmed to 25-40°C and 0.5 parts of a 10 percent solution of sodium erythorbate was injected into the reaction mixture.

The mixture typically began to polymerize within 5 minutes. The maximum temperature of the reaction mass was controlled between 80°C and 100°C, preferably between 80°C and 90°C, by pulling a vacuum on the reaction vessel. After the polymerization exotherm subsided, the vacuum was relieved with nitrogen and the reaction mass was agitated further at 60°C-70°C for 3 or more hours.

The reaction gel mass was removed from the vessel and if necessary was further sized by extrusion through a die of the appropriate size. If employed, the second crosslinking agent was added to the gel by agitating the gel in an appropriate blender while adding the second covalent crosslinking agent.

The gel was dried by passing heated air (165-185°C) through the gel bed for 20-40 minutes. Control of the drying time and temperature was necessary to obtain the desired gel bed permeability. After drying, the moisture content of the gel was typically 1-3

wt. percent when determined gravimetrically after heating the dried polymer in an oven at 105°C for three hours.

The dried product was ground in a roll crusher and screened to obtain the desired particle size distribution.

5 Comparative Experiments 1-5 (not an embodiment of the invention)

Polymers were prepared using Procedure A with varying amounts of SARTOMER #9035 (in ppm based on acrylic acid monomer, hereinafter BOA) without a second crosslinking agent. The samples were dried for 30 minutes at 175°C.

10 Table I: Control Experiments

Comp. Expt.	#9035 (ppm)	AC (g/g)	Gel bed permeability
1	10,000	26.6	$4 \times 10^{-9} \text{ cm}^2$
2	15,000	24.9	$7 \times 10^{-9} \text{ cm}^2$
3	20,000	23.4	$10 \times 10^{-9} \text{ cm}^2$
4	30,000	22.0	$15 \times 10^{-9} \text{ cm}^2$
5	50,000	21.4	$12 \times 10^{-9} \text{ cm}^2$

These results show that it took extremely high levels of a single polyvinyl crosslinker to achieve low absorption capacity. Such high levels are cost prohibitive from an industrial viewpoint.

15 Example 6

A sample of gel was made using Procedure A with a SARTOMER #9035 level of 8.300 ppm BOA and was collected prior to drying. The gel was then treated with 10,200 ppm of glycerol (BOA) and the glycerol was allowed to diffuse into the hydrogel such that it was substantially uniformly distributed. The gel was dried at 170°C for a total of 36 minutes.

20 Example 7

A sample of gel was prepared using Procedure A with a SARTOMER #9035 level of 8.300 ppm (BOA) and was collected prior to drying. The gel was then treated with 13,000 ppm of glycerol (BOA). The gel was dried at 175°C for 35 minutes.

Example 8

This sample was prepared using Procedure A with 6,000 ppm SARTOMER #9035 BOA. Additionally, 20,000 ppm of hydroxyethylmethacrylate (BOA) was added to the monomer mix. The sample was dried for 30 minutes at 180°C.

5 Example 9

A sample of gel was made using Procedure A with a SARTOMER #9035 level of 8,300 ppm BOA. The hydrogel was then treated with 18,000 ppm of glycerol (BOA) and the glycerol was allowed to diffuse into the hydrogel such that it was
 10 substantially uniformly distributed. The gel was dried for a total of 30 minutes to a final temperature of approximately 180°C. The dried product was ground to the desired particle size. Five-hundred parts of the ground product were charged to a suitable blender and 20 parts of an aqueous solution containing 5.6 parts of aluminum sulfate were sprayed onto the product along with 0.5 part of an aqueous solution containing 0.25 part of VORANOL 230-
 15 238 polyol (The Dow Chemical Company) as a dedusting agent.

Example 10

A sample of gel was made using Procedure A with a SARTOMER #9035 level of 8,300 ppm BOA. The hydrogel was then treated with 1,560 ppm of glycerol (BOA)
 20 and the glycerol was allowed to diffuse into the hydrogel such that it was substantially uniformly distributed. The gel was dried for a total of 30 minutes to a final temperature of approximately 180°C. The dried product was ground to the desired particle size. The ground product was further heat-treated at 205°C for 50 minutes. Five-hundred parts of the heat-treated product were charged to a suitable blender and 15 parts of an aqueous solution
 25 containing 4.2 parts of aluminum sulfate were sprayed onto the product along with 0.5 part of an aqueous solution containing 0.25 part of VORANOL 230-238 polyol as a dedusting agent.

Table II: Use of Combinations of Crosslinkers

	SARTOMER #9035 (ppm BOA)	Second Crosslink ing Agent (ppm BOA)	AC (g/g)	Gel Bed Permeability ($\times 10^{-9}$ cm ²)
Example 6	8,300	10,200	25.0	7
Example 7	8,300	13,000	21.0	13
Example 8	6,000	20,000	13.8	72
Example 9	8,300	18,000	22.1	16
Example 10	8,300	1,560	23.6	35

Comparative Experiment 11 and Examples 12-15

- Polymers were prepared using Procedure A with the SARTOMER #9035 levels, glycerol levels, and drying times (@ 175°C) shown in the table below. The resulting absorption capacities (AC) and gel bed permeabilities (GBP, $\times 10^{-9} \text{ cm}^2$) are given in Table III.

Table III: Effect of Glycerin and Drying Time

	SARTOMER #9035 (ppm BOA)	Glycerol (ppm BOA)	Drying Time (min)	AC (g/g)	GBP ($\times 10^{-9} \text{ cm}^2$)
C.E. 11*	5,000	3,000	30	26.1	3
Ex. 12	5,000	9,000	30	23.2	6
Ex. 13	5,000	12,000	30	21.4	11
Ex. 14	5,000	12,000	37.5	18.4	20
Ex. 15	5,000	12,000	45	16.5	26

* not an embodiment of the invention

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CLAIMS:

1. A process for the preparation of water-swellable, water-insoluble polymer particles having high gel bed permeability, the process comprising crosslinking the polymer using at least 2 covalent crosslinking agents, the crosslinking agents comprising a polyvinyl first crosslinking agent and a hydroxyl-containing second crosslinking agent, under conditions such that there is formed a polymer that is substantially uniformly crosslinked, and that has a gel bed permeability of at least $5 \times 10^{-9} \text{ cm}^2$ and an absorption capacity of less than 26 g/g.
2. The process of Claim 1 wherein the absorption capacity is less than 24 g/g.
3. The process of Claim 1 wherein the absorption capacity is less than 22 g/g.
4. The process of Claim 1 further comprising subsequently treating the polymer with from 0.25 to 4 weight parts of aluminum sulfate in aqueous solution per hundred weight parts of polymer.
5. The process of Claim 1 wherein the second crosslinking agent is selected from the group consisting of glycerin, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, polyglycerin, trimethylolpropane, polyethylene glycol, and polypropylene glycol-polyethylene glycol copolymers, and 2-hydroxyethyl (meth)acrylate, polyethylene glycol monomethacrylate, glycidyl methacrylate, and allyl glycidyl ether.
6. The process of Claim 1 wherein the polymer is selected from the group consisting essentially of the hydrolyzates of starch-acrylonitrile graft copolymers, partially neutralized products of starch-acrylic acid or starch-polyvinyl alcohol graft copolymers, saponification products of vinyl acetate acrylic ester copolymers, derivatives of copolymers of isobutylene and maleic anhydride, hydrolyzates of acrylonitrile carboxymethyl cellulose, hydrolyzates of acrylamide copolymers, and partially neutralized products of polyacrylic acids.
7. The process of Claim 1 wherein the polymer is partially neutralized polyacrylic acid.
8. The process of Claim 1 wherein the first crosslinking agent is selected from the group consisting of: diacrylates and dimethacrylates of ethylene glycol, diethylene

glycol, triethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane and pentaerythritol; triacrylates and trimethacrylates of trimethylolpropane and pentaerythritol; highly ethoxylated trimethylol propane triacrylate; tetracrylates and tetramethacrylates of pentaerythritol; allyl methacrylate; and
5 tetraallyloxyethane.

9. A polymer prepared by the process of Claim 1.

10. An absorbent article comprising the polymer of Claim 9.

11. The article of Claim 10 which is a diaper or part of a diaper wherein the weight ratio of superabsorbent polymer composition to fluff is at least 0.3.

10 12. An absorbent article comprising the polymer of Claim 11.

13. The article of Claim 12 which is a diaper or part of a diaper wherein the ratio of superabsorbent polymer composition to fluff is at least 0.3.

14. A water-swellaable, water-insoluble polymer having a substantially uniform crosslink density and a gel bed permeability of at least $20 \times 10^{-9} \text{ cm}^2$ and an
15 absorption capacity of less than 26 g/g.

15. An absorbent article comprising the polymer of Claim 14.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/35082

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61L15/24 A61L15/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J C08L A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 49221 A (GARTNER HERBERT A ;DOW CHEMICAL CO (US); FIALKOWSKI MICHAEL (US);) 5 November 1998 (1998-11-05) page 5, line 30 -page 6, line 16 page 8, line 28 -page 9, line 2 page 11, line 16 - line 24 examples 14-30; tables IV-VII claims	1-15
X	WO 94 20547 A (DOW CHEMICAL CO ;BURGERT JOSEF H (DE); GARTNER HERBERT A (DE); CHR) 15 September 1994 (1994-09-15) examples 31-56; tables 6-8 claims	1-15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 00/35082

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 837 076 A (NIPPON CATALYTIC CHEM IND)</p> <p>22 April 1998 (1998-04-22)</p> <p>page 5, line 30 - line 40</p> <p>page 10, line 57 -page 11, line 6</p> <p>-----</p>	1-3,5-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 00/35082

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